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Racemic Charge-Transfer Complexes of Helical Polycyclic Aromatic Hydrocarbon Molecule†

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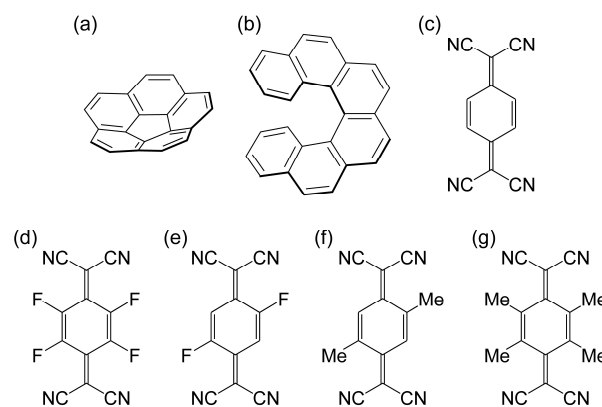
Singles crystals of racemic charge-transfer complexes comprising a helical polycyclic aromatic hydrocarbon molecule, [6]helicene, as the electron donor (D) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) analogs as the electron acceptor (A) were obtained by either co-sublimation or solvent evaporation. All complexes consist of heterochiral DA-type alternating π -columns with a [...(*P*)-[6]helicene...TCNQ...(M)-[6]helicene...TCNQ...] repeating unit, which show a peculiar wavy feature primarily related to the nonplanar geometry of [6]helicene molecules. [6]Helicene molecules form a two-dimensional sheet intersecting the columns, and the molecular arrangement (namely, either homochiral or heterochiral arrangement) in the sheets depends on the TCNQ analog. Theoretical calculations were carried out to discuss the origin of the molecular deformation of [6]helicene molecules in the CT solids in terms of intermolecular interactions.

Introduction

For more than half a century, polycyclic aromatic hydrocarbons (PAHs) have been widely utilised in organic electronics, e.g., photovoltaics, field-effect transistors, and solar cells.^{1–3} Intermolecular π - π interactions promote the self-assembly of PAH molecules into columnar stacks; therefore, these interactions play a crucial role in the π -electronic properties of the aggregates. Furthermore, co-crystallization with electron-donating (D) or -accepting (A) counter molecules, with diverse combinations, utilizing charge-transfer (CT) interactions has afforded a variety of exotic PAH-based electronic materials, e.g., metals and superconductors.^{4–6}

Recently, nonplanar π -conjugated molecules have attracted attention as components for the assembly of an unconventional π -electron network.^{7–9} Two main approaches are utilised to produce nonplanar PAH molecules: endoskeletal and exoskeletal approaches. In the former approach, a nonhexagonal ring is present inside hexagonal skeletons (e.g., [*n*]circulenes;¹⁰ Scheme 1a), while the latter approach exploits steric hindrance because of crowdedness (e.g., [*n*]helicenes;^{11,12} Scheme 1b). With respect to the former type, our group has reported the first corannulene-based CT solid using 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ; Scheme 1c), (corannulene)₂TCNQ; in this solid, the CT interaction with an adjacent TCNQ molecule on the convex side of the corannulene is apparently greater than that on the concave side.¹³ In this study, four

racemic CT complexes based on [6]helicene, which is categorised into the latter group, were prepared using various TCNQ analogs (Scheme 1c–1f), and their optical and crystallographic properties, in addition to theoretical calculations, were investigated. For [*n*]helicenes, increasing efforts continue to be devoted to achieving control crystalline forms of racemates, i.e., racemic mixtures (conglomerates), racemic compounds, or solid solutions, by changing molecular structures, counter components, and crystallization processes.^{11,12}



Scheme 1 Molecular structures of (a) corannulene ([5]circulene), (b) [6]helicene, (c) TCNQ, (d) F₄TCNQ, (e) F₂TCNQ, (f) Me₂TCNQ, and (g) Me₄TCNQ.

Results and Discussion

Crystal Growth

Commercial racemic [6]helicene was used as received. CT complexes with TCNQ analogs, ([6]helicene)(F₄TCNQ) (**1**), ([6]helicene)(F₂TCNQ) (**2**), and ([6]helicene)(Me₂TCNQ) (**4**), were prepared by co-sublimation, whereas a CT complex with parent

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† Electronic Supplementary Information (ESI) available: Infrared spectra and X-ray crystallographic data in CIF format for **1–4**. See DOI: 10.1039/x0xx00000x

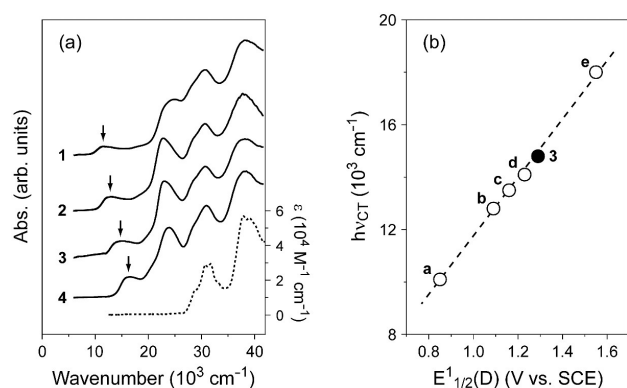


Fig. 1 (a) Electronic absorption spectra of **1–4** measured on KBr pellets (solid lines) together with pristine [6]helicene in a 10^{-5} M chloroform solution (dotted line). Arrows denote the CT absorption bands. (b) Plot of CT energy ($h\nu_{CT}$) against the first redox potential of PAH molecules ($E^{1/2}(D)$) in the TCNQ complexes (a: (perylene)(TCNQ),¹⁷ b: (anthracene)(TCNQ),¹⁸ c: (pyrene)(TCNQ),¹⁹ d: (coronene)(TCNQ),^{20,21} e: (triphenylene)₂(TCNQ)(toluene)²²).

TCNQ, ([6]helicene)(TCNQ) (**3**),¹⁴ was prepared by solvent evaporation (see Experimental section). Notably, co-sublimation and solvent evaporation using Me₂TCNQ (Scheme 1g) with a weak electron-accepting ability ($E^{1/2}(A) = -0.05$ V vs. saturated calomel electrode (SCE)) afforded no trace of the CT complex.

Charge Transfer

Fig. 1a shows the electronic absorption spectra of **1–4** dispersed in KBr pellets. A low-lying band, corresponding to the intermolecular CT transition, was observed at $h\nu_{CT} = 11\text{--}17 \times 10^3 \text{ cm}^{-1}$ in addition to the intramolecular transition bands of the component molecules at greater than $20 \times 10^3 \text{ cm}^{-1}$. The low-energy band provides clear evidence of the CT interactions between [6]helicene and TCNQ analogs in solids. The $h\nu_{CT}$ value steadily decreases with the increase in the electron-accepting ability of the TCNQ analogs (Table 1). This relationship is indicative of a neutral ground state with alternating π -columns,¹⁵ which is in agreement with the high first redox potential of [6]helicene ($E^{1/2}(D) = 1.29$ V vs. SCE¹⁶ relative to the $E^{1/2}(A)$ values of the TCNQ analogs. Notably, complex **3** formed with parent TCNQ lies on a straight line via the application of a least-squares method to the plots of $h\nu_{CT}$ against $E^{1/2}(D)$ of typical planar PAH

Table 1 Typical parameters for **1–4**

Complex	1	2	3	4	(M)-[6]helicene
Acceptor (A)	F ₄ TCNQ	F ₂ TCNQ	TCNQ	Me ₂ TCNQ	—
$E^{1/2}(A)$ (V vs. SCE) ^a	0.60	0.41	0.22	0.15	—
$h\nu_{CT}$ (10^3 cm^{-1}) ^b	11.6	12.9	14.8	16.5	—
d (Å) ^c	4.39	4.20	4.19, 4.20	4.12	4.48
γ (°) ^d	57.6	47.0	45.1, 46.2	41.8	59.5

^a First redox potential of TCNQ analogs (SCE: saturated calomel electrode). ^b CT absorption band measured on KBr pellets. ^c Distance between the terminal benzene centroids in a [6]helicene molecule based on the crystallographic data at 100 K. ^d Angle between the planes of the terminal benzene rings in a [6]helicene molecule based on the crystallographic data at 100 K.

Table 2 Crystallographic data of **1–4**

Complex	1	2	3	4	(M)-[6]helicene
Formula	C ₃₈ H ₁₆ F ₄ N ₄	C ₃₈ H ₁₆ F ₂ N ₄	C ₃₈ H ₂₀ N ₄	C ₄₀ H ₂₄ N ₄	C ₂₆ H ₁₆
Formula weight	604.57	568.58	532.60	560.66	328.41
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>Pbcn</i>	<i>P2₁/n</i>	<i>P2₁/c</i>	<i>C2/c</i>	<i>P2₁2₁2₁</i>
Crystal size, mm ³	0.37 × 0.32 × 0.10	0.38 × 0.19 × 0.11	0.47 × 0.06 × 0.05	0.49 × 0.46 × 0.40	0.36 × 0.24 × 0.06
a , Å	7.1454(4)	8.3747(4)	8.2077(5)	14.4593(7)	7.3079(3)
b , Å	17.2601(9)	16.7659(8)	33.7880(19)	11.4032(6)	12.9491(6)
c , Å	22.2970(11)	19.2823(9)	19.3173(11)	17.8273(9)	17.4393(8)
α , deg	90	90	90	90	90
β , deg	90	90.488(1)	92.882(1)	102.652(1)	90
γ , deg	90	90	90	90	90
V , Å ³	2749.9(3)	2707.3(2)	5350.3(5)	2868.0(3)	1650.3(1)
Z	4	4	8	4	4
Temperature, K	100	100	100	100	100
d_{alc} , g cm ⁻³	1.460	1.395	1.322	1.298	1.322
μ (Mo K α), mm ⁻¹	0.106	0.093	0.079	0.077	0.075
Refins used	2811	5528	10950	2929	3371
Refined params	209	404	757	201	235
R_1 (for $I > 2\sigma(I)$) ^a	0.0321	0.0391	0.0482	0.0343	0.0294
wR_2 (for all data) ^b	0.0915	0.0991	0.1045	0.1016	0.0724
GOF on F^2	1.045	1.019	0.975	1.096	1.058
CCDC number	1533425	1533426	1533427	1533428	1535631

^a $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$.

molecules (perylene,¹⁷ anthracene,¹⁸ pyrene,¹⁹ coronene,^{20,21} and triphenylene²²) for their TCNQ complexes (Fig. 1b).

Infrared spectra of **1–4** are readily assigned by the superposition of those of the component molecules, which also supports the neutral ground state (Fig. S1 in ESI†). For complex **1** formed with the strongest electron acceptor, F₄TCNQ, the *b*_{1u} *ν*_{C=C} mode (1591 cm^{−1}) is shifted to a low frequency by 9 cm^{−1} relative to that of neutral F₄TCNQ (1600 cm^{−1}). Assuming that the reduction state of F₄TCNQ molecule is linearly correlated with the *ν*_{C=C} shift, namely $\delta = -(\omega_{\text{obs}} - \omega_0)/(\omega_1 - \omega_0)$, where ω_{obs} , ω_0 , and ω_1 denote the *ν*_{C=C} mode frequencies of a CT complex, neutral F₄TCNQ, and monoanionic F₄TCNQ, respectively,²³ the charge of the F₄TCNQ molecules in **1** was estimated to be as low as approximately −0.1.

Crystal Structure

Crystal structures of **1–4** were determined at 100 K (Table 2). Despite their distinct crystal lattices, all complexes exhibit 1:1 stoichiometry, with peculiar wavy DA-type alternating π -columns. In the column, [6]helicene and TCNQ analogs are arranged in a heterochiral manner, with a $[\cdots(P)\text{-}[6]\text{helicene}\cdots\text{TCNQ}\cdots(M)\text{-}[6]\text{helicene}\cdots\text{TCNQ}\cdots]$ repeating unit. These complexes are racemates, and no spontaneous enantiomer resolution occurred during crystallization. Complex **3** prepared in this study exhibits a structure identical to that reported by Ermer:¹³ two [6]helicene and two TCNQ molecules are crystallographically independent, and the charges of the TCNQ molecules were estimated to be −0.15(4) and −0.12(3) on the basis of the intramolecular bond lengths.²⁴

Complex **1** belongs to the orthorhombic system with space group *Pbcn*, and the asymmetric unit contains a half [6]helicene and a half F₄TCNQ. Adjacent (*P*)-[6]helicene and (*M*)-[6]helicene within the column are related by an inversion centre, whereas F₄TCNQ is located on an inversion centre. Distance between the terminal benzene centroids (*d*) and angle between the planes of the terminal benzene rings (γ) in [6]helicene were estimated as 4.39 Å and 57.6°, respectively. The contraction of [6]helicene molecules in **1** relative to those in the enantiomeric crystal (4.48 Å and 59.5°, respectively; Table 2)^{25,26} is possibly related to Wallach's rule,^{27,28} which suggests denser packing in racemic crystals compared to their chiral conglomerates. From bond length analysis,^{24,29} the charge of F₄TCNQ was estimated as −0.05(3), which is in good agreement with that expected from the infrared spectrum (*ca.* −0.1).

The complex involves wavy DA-type alternating π -columns along the *c* axis (Fig. 2a). In the column, a terminal benzene ring of [6]helicene and a quinonoid ring of F₄TCNQ exhibits a ring-over-bond overlap pattern (Fig. 2b), and are arranged in a nonparallel fashion with a dihedral angle of 3.98°. At *z* ~ 0.25 and 0.75, [6]helicene molecules form heterochiral sheets comprising equimolar amounts of (*P*)-[6]helicene and (*M*)-[6]helicene. Each F₄TCNQ molecule is connected to two adjacent [6]helicene molecules (one (*P*)-[6]helicene and one (*M*)-[6]helicene) through C–H⋯F hydrogen bonds (H7⋯F1: 2.61 Å, H8⋯F1: 2.48 Å vs. sum of van der Waals radii: 2.67 Å;³⁰ Fig. 2c) along the molecular short axis to form an infinite array along the [4 0 1] or [4 0 $\bar{1}$] direction. In addition, each F₄TCNQ molecule interacts with two adjacent [6]helicene molecules (one (*P*)-[6]helicene and one (*M*)-[6]helicene) along the molecular long axis through C–H⋯N hydrogen bonds (H1⋯N2: 2.55 Å vs. sum of van der Waals radii: 2.75 Å³⁰). As shown in Fig. 2d, the hydrogen-

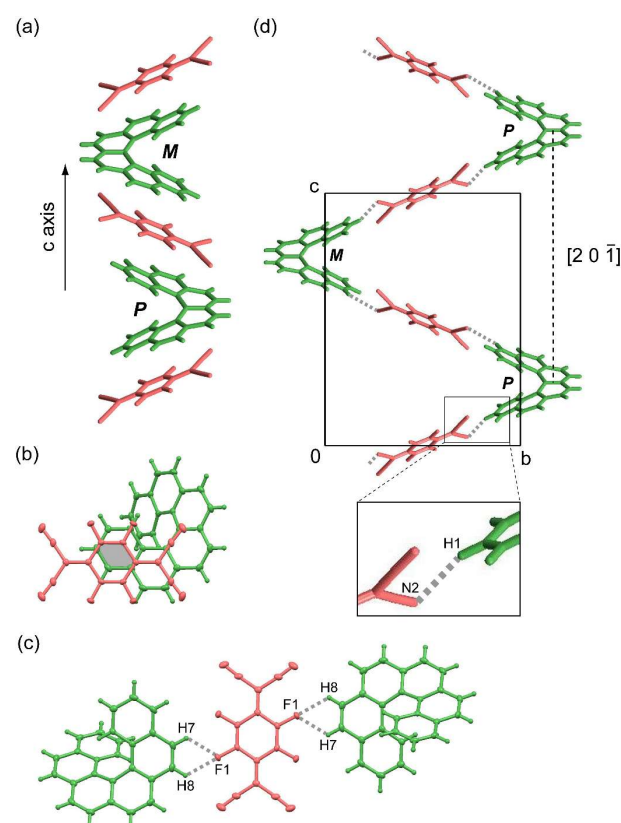


Fig. 2 (a) DA-type alternating π -column in **1** viewed along the *c* axis, where *P* and *M* indicate (*P*)- and (*M*)-[6]helicene molecules, respectively. (b) Overlap pattern of adjacent [6]helicene and F₄TCNQ within a column viewed perpendicular to the molecular plane of F₄TCNQ in **1**. See text for the grey area. (c) Short C–H⋯F contacts with H⋯F distances of less than the sum of the van der Waals radii (2.67 Å; grey dotted lines) around one F₄TCNQ molecule in **1**. (d) Supramolecular helix through C–H⋯N hydrogen bonds (grey dotted lines) viewed along the *a* axis, where a helix extending along the [2 0 1] direction is shown. [6]Helicene and F₄TCNQ molecules are shown in green and red, respectively.

bonding interactions afford an infinite supramolecular helix with a $[\cdots(P)\text{-}[6]\text{helicene}\cdots\text{F}_4\text{TCNQ}\cdots(M)\text{-}[6]\text{helicene}\cdots\text{F}_4\text{TCNQ}\cdots]$ repeating unit of 26.5 Å along the [2 0 1] or [2 0 $\bar{1}$] direction.

Complex **2** crystallises in a monoclinic lattice with space group *P2₁/n*, and each of [6]helicene and F₂TCNQ is crystallographically independent. The *d* and γ values of [6]helicene were estimated as 4.20 Å and 47.0°, respectively, and fluorine atoms in F₂TCNQ were orientationally disordered over two distinct orientations, 2,5- and 3,6-positions, with an occupancy ratio of 93/7.

The wavy alternating π -columns shown in Fig. 3a run along the [1 0 1] direction. Each F₂TCNQ exhibits a ring-over-ring overlap with a second terminal benzene ring of [6]helicene with a dihedral angle of 2.32° on one side, whereas it exhibits a ring-over-bond overlap on the other side (Fig. 3b). Unlike **1**, [6]helicene molecules in **2** form homochiral sheets at *z* ~ 0.25 and 0.75 for (*P*)- and (*M*)-type enantiomers, respectively, which are related by an inversion centre. Whereas fluorine atoms in F₂TCNQ form no short interatomic contacts with adjacent [6]helicene molecules in contrast to **1**, intermolecular C–H⋯N hydrogen bonds (H7⋯N1: 2.71 Å,

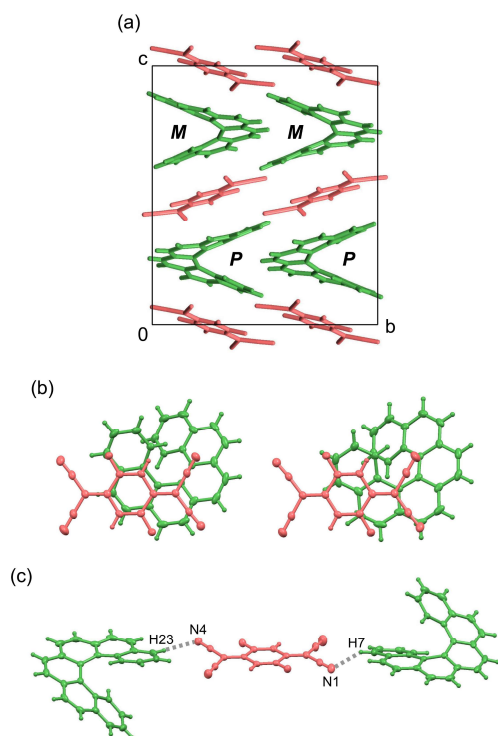


Fig. 3 (a) Crystal structure of **2** viewed along the *a* axis, where *P* and *M* indicate (*P*)- and (*M*)-[6]helicene molecules, respectively. (b) Overlap pattern of adjacent [6]helicene and F₂TCNQ within a column viewed perpendicular to the molecular plane of F₂TCNQ in **2**. (c) Short C–H...N contacts with H...N distances of less than the sum of the van der Waals radii (2.75 Å; grey dotted lines) around one F₂TCNQ molecule in **2**. Only the major orientation of the disordered F₂TCNQ is shown, and [6]helicene and F₂TCNQ molecules are shown in green and red, respectively.

H23...N4: 2.57 Å; Fig. 3c) result in the formation of an infinite supramolecular helix with a [...(*P*)-[6]helicene...F₂TCNQ...(M)-[6]helicene...F₂TCNQ...] repeating unit of 31.5 Å along the [3 0 1] or [3 0 $\bar{1}$] direction.

Complex **4** also belongs to the monoclinic system with space group *C2/c*, and the asymmetric unit contains a half [6]helicene and a half Me₂TCNQ. Adjacent (*P*)-[6]helicene and (*M*)-[6]helicene within the column are related by an inversion centre and form homochiral sheets at *z* ~ 0.25 and 0.75, respectively. Notably, the lowest *d* and γ values (4.12 Å and 41.8°, respectively) were observed.

The wavy alternating π -columns (pink area in Fig. 4a) run along the *c* axis, in which adjacent [6]helicene and Me₂TCNQ molecules exhibit a ring-over-bond overlap fashion (Fig. 4b). In contrast to other complexes, a bulky methyl group in Me₂TCNQ, which is located on an inversion centre, approaches the adjacent helical core, affording close packing (Fig. 4c). As indicated by the blue area in Fig. 4a, this complex forms infinite supramolecular helices with a [...(*P*)-[6]helicene...Me₂TCNQ...(M)-[6]helicene...Me₂TCNQ...] repeating unit of 17.8 Å through C–H...N hydrogen bonds (H1...N1: 2.64 Å). Adjacent helices along the *a* axis are connected through another C–H...N hydrogen bonds (H7...N1: 2.60 Å). Considering that the helices run along the *c* axis, each of the [6]helicene and Me₂TCNQ molecules within the column comprises the same helix.

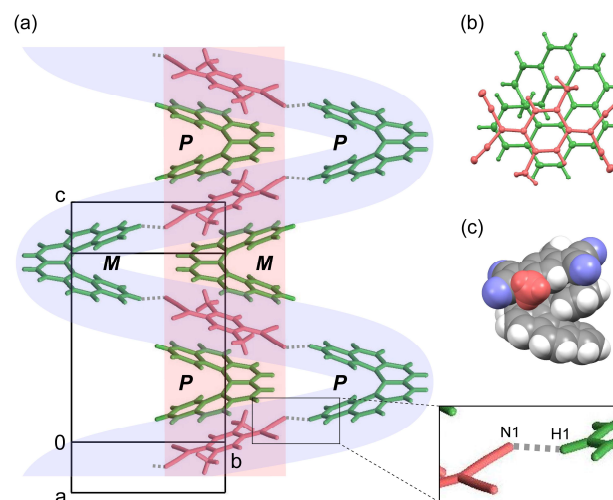


Fig. 4 (a) Crystal structure of **4**, where *P* and *M* indicate (*P*)- and (*M*)-[6]helicene molecules, respectively. Pink and blue areas denote the DA-type alternating π -column and supramolecular helix, respectively, both of which run along the *c* axis. Grey dotted lines denote C–H...N hydrogen bonds. (b) Overlap pattern of adjacent [6]helicene and Me₂TCNQ within a column viewed perpendicular to the molecular plane of Me₂TCNQ in **4**. (c) Molecular packing of a pair of [6]helicene and Me₂TCNQ molecules, where a methyl group near the [6]helicene molecule is indicated in red. [6]Helicene and Me₂TCNQ molecules in (a) and (b) are shown in green and red, respectively.

Molecular deformation

Thus far, the molecular geometry of [6]helicene has been modified via the coordination of a silver(I) ion³¹ and the functionalization of terminal benzene rings.³² Fig. 5 shows the plots of *d* and γ values as a function of the *E*^{1/2}(A) values of TCNQ analogs for **1–4**. The [6]helicene molecules are seemingly elongated with the increase in the electron-accepting ability of TCNQ analogs; namely, intermolecular CT interactions exhibit beneficial effects on the molecular geometry of [6]helicene in the solid state. However, our density functional theory (DFT) calculations at the CAM-B3LYP-D3(BJ)/spAug-cc-pVDZ level of theory predicted that the cationization of C₂-symmetric [6]helicene marginally affects molecular geometry; the *d* and γ values of the [6]helicene monocation (4.21 Å and 47.2°, respectively) are similar to those of neutral [6]helicene (4.25 Å and 48.5°, respectively).

To help understand the molecular deformation experimentally observed, we turn to the relative configuration between the benzene ring(s) of [6]helicene and a quinonoid ring of TCNQ analogs. In complex **4**, a methyl group of Me₂TCNQ penetrates the helical core of an adjacent [6]helicene within the column, and a hydrogen atom in the methyl group forms a C–H... π hydrogen bond^{33,34} at a distance of 2.92 Å with a benzene ring of [6]helicene. Such a complementary interaction inevitably plays an important role in the close packing, possibly leading to the decreased *d* and γ values. On the other hand, the increased *d* and γ values in **1** are possibly related to the overlap ratio, which is defined as the ratio of the overlap area to the area of a quinonoid ring area viewed perpendicular to the molecular plane of TCNQ analogs (For example, a grey area shown in Fig. 2b); the

overlap ratio in **1** (54%) is apparently less than those in **2** (58%) and **3** (60 and 61%). Although the factors that determine the overlap mode in these solids remain unclear, the depressed intermolecular π - π interactions between [6]helicene and F₄TCNQ molecules within the column possibly result in the elongation of [6]helicene molecules in **1**.

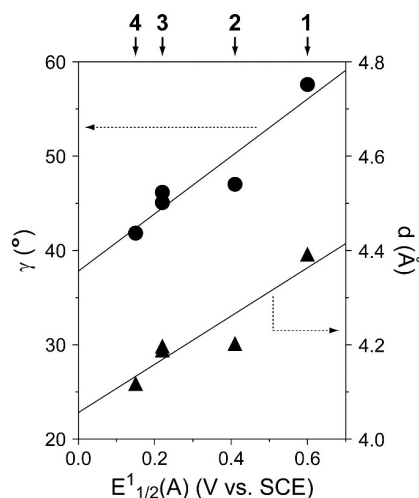


Fig. 5 Plots of distance between the terminal benzene centroids (d ; triangle) and angle between the planes of the terminal benzene rings (γ ; circle) in a [6]helicene molecule against the first redox potential of the TCNQ analogs ($E^{1/2}(A)$). Solid lines denote the least-square fits of the data.

Conclusions

The combination of racemic [6]helicene and TCNQ analogs yields racemic neutral CT complexes instead of chiral conglomerates. All complexes consist of heterochiral DA-type alternating π -columns with a wavy structure associated with the helical structure of [6]helicene. The small π - π overlap between the adjacent [6]helicene and F₄TCNQ results in the elongation of [6]helicene, whereas the complementary interactions via C-H $\cdots\pi$ hydrogen bonds between [6]helicene and Me₂TCNQ within the column contracts [6]helicene. Further studies will be focused on the exploration of ionic CT complexes formed with (partially) cationic [6]helicene molecules not only to construct an unprecedented higher-dimensional π -conduction network but also to elucidate the relationship between the molecular geometry of [6]helicene and electronic properties of the CT solids.

Experimental section

General details

1,1,2-Trichloroethane and chloroform were distilled from CaH₂ prior to use. Racemic [6]helicene (Lach-Ner, Czech Republic) was used as received, whereas TCNQ analogs were purified by recrystallization and/or sublimation after being synthesised by our research group or purchased commercially.

Syntheses of **1**, **2**, and **4**

Equimolar amounts of racemic [6]helicene (0.015 mmol) and the TCNQ analog (0.015 mmol) were ground together in an agate mortar

and transferred into a borosilicate glass tube with a diameter of 12 mm. After sealing under vacuum (5×10^{-5} Torr), the 13-cm-long tube was placed in a two-zone furnace with a temperature gradient from 201 °C (sample side) to 149 °C (opposite side). After heating for 2–4 days, black thick plate crystals of **1**, black hexagonal bifrustum crystals of **2**, and black block crystals of **4** were grown on the opposite side in the tube. Yield: 30–50%.

Synthesis of **3**

Black rod crystals of **3** were obtained by the slow evaporation of a 1,1,2-trichloroethane solution (10 mL) containing equimolar amounts of racemic [6]helicene (0.01 mmol) and TCNQ (0.01 mmol). Yield: ca. 80%.

Spectroscopy

UV-Vis-NIR absorption spectra were measured on KBr pellets (3.8 – 42×10^3 cm⁻¹) or in a chloroform solution (12 – 50×10^3 cm⁻¹) using a Shimadzu UV-3100 spectrophotometer. Infrared transmission spectra were measured on KBr pellets using a Shimadzu Prestige-21 spectrophotometer (380 – 7800 cm⁻¹).

X-Ray structural analysis

Single-crystal X-ray diffraction experiments were performed on a CCD-type diffractometer (Bruker SMART APEX II) with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 100 K. A single crystal was mounted on a glass capillary and cooled by a stream of cooled nitrogen gas. The crystal structures solved by a direct method using the SIR2004 program³⁵ were refined by a full-matrix least-squares method on F^2 using SHELXL.³⁶ All non-hydrogen atoms were anisotropically refined. The positional parameters of the hydrogen atoms were calculated under the assumption of fixed C–H bond lengths of 0.93 and 0.96 Å with sp² and sp³ configurations, respectively, of the parent atoms. In the refinement procedures, isotropic temperature factors with a magnitude 1.2-fold greater than that of the equivalent temperature factors of the parent atoms were applied to the hydrogen atoms.

Computational details

DFT calculations were performed using the CAM-B3LYP,³⁷ CAM-B3LYP-D3(BJ),^{37,38} and M11³⁹ functionals in combination with the spAug-cc-pVDZ basis set.^{40,41} Full geometry optimization, with “Opt = Tight” specified, was conducted for C₂-symmetric (*P*)-[6]helicene⁰ as well as C₂- and C₁-symmetric (*P*)-[6]helicene^{•+}. Note that all of the functionals found one imaginary frequency in C₂-symmetric (*P*)-[6]helicene^{•+}, indicating a transition state. The stability of the wave function was confirmed by specifying the “Stable=Opt” keyword. The “Int=SuperFineGrid” keyword was specified throughout the current DFT calculations. All computations were performed with the Gaussian 09 program package.⁴²

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